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Metal and ligand control in di- and octa-nuclear cluster formation†

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Reaction of doubly negatively charged *m*-pyridinediyl spacered bis-bidentate ligands with iron(III) chloride in the presence of alkaline, alkaline earth, and rare earth metal cations (M^{n+}) yielded {2}-iron cryptates $\{M\subset[Fe_2(L)_3]\}^{n+}$. The mono-, di-, and tri-valent guest cations are endohedrally encapsulated in the cavity of the bicyclic dinuclear host. In contrast, the ligands reacted with Mn^{2+}, Co^{2+}, and Cd^{2+} (M^{II}) cations as pentadentate tritopic chelators to give octanuclear complexes $[M^{II}_8O_2(L)_6]$. Similarly, a topological equivalent pentadentate tritopic ligand L′ in the presence of Zn^{2+} cations afforded the octanuclear cluster $[Zn_8O_2(L')_6]$. However its reaction with iron(III) chloride and alkaline, alkaline earth, and rare earth metal cations did not lead to products of type $\{M\subset[Fe_2(L)_3]\}^{n+}$.

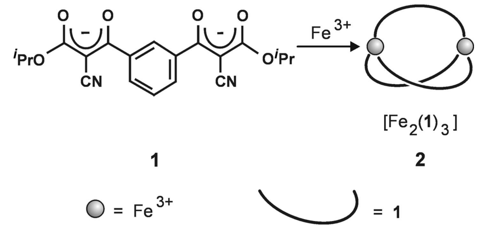
Introduction

Perhaps the earliest triple helicate to be characterized is that formed with rhodotorulic acid, the dihydroxamate siderophore produced by the yeast *Rhodotorula pilimanae*.[2] Subsequently, a related synthetic iron(III) triple helicate based on a tetradentate 1,2-dihydroxypyridinone was synthesized and its molecular structure characterized by X-ray crystallography.[3] The rules governing coordination chemistry for the generation of {2}-metalla-cryptands (= dinuclear triple helicates) have successfully been employed for the preparation of numerous examples.[4–9]

The formation of a dimetallic triple-stranded helicate is associated with the generation of a macrobicyclic cavity. The host/guest properties of these self-assembled cavities strongly depend on the possible interaction between spacer and guest and the electronic charge of the {2}-metalla-cryptand.[4] Notably, most of the macrobicyclic host cavities remain unoccupied and only recently it was shown that alkyl-bridged bis(catecholate) ligands such as $(L^1)^{4-}$ and $(L^2)^{4-}$ [H_4L^1 = bis(2,3-dihydroxyphenyl)methane, H_4L^2 = 1,2-bis(2,3-dihydroxyphenyl)ethane] react with $[TiO(acac)_2]$ and Li_2CO_3 to give two principally different products.[10] With H_4L^1 an achiral *meso*-metalla-cryptand (mesocate)[11] (Δ,Λ)-$Li[Li_3\cap(Ti_2L^1_3)]$ was isolated. In the tetraanionic $(Ti_2L^1_3)^{4-}$ core two Ti^{4+} cations are linked by three bis(bidentate) $(L^1)^{4-}$ ligands. Thus, each titanium(IV) ion is octahedrally coordinated by six oxygen atoms. Three of the four Li^+ cations are exohedrally capping the squares of the trigonal prism formed by the six oxygen atoms. Charge compensation is achieved by the remaining Li^+ cation.

On the contrary, H_4L^2 yielded racemic (Δ,Δ)/(Λ,Λ)-$Li_3[Li\subset(Ti_2L^2_3)]$. In this case, the tetraanionic $(Ti_2L^2_3)^{4-}$ core encapsulated endohedrally one of the lithium cations in its cavity. The remaining three Li^+ cations connect the $(Ti_2L^2_3)^{4-}$ cores to give a polymeric overall structure in the solid state.

A racemic {2}-metalla-cryptand (Δ,Δ)/(Λ,Λ)-$[Fe_2(\mathbf{1})_3]$ **2** was generated from the doubly negatively charged bis-bidentate ligand **1** with iron(III) chloride (Scheme 1).[12] In this case the neutral $[Fe_2(\mathbf{1})_3]$ core remained unoccupied. We now report on extended syntheses of topologically equivalent {2}-metalla-cryptates with endohedral cation encapsulation in the cavity simply by replacing the *m*-phenylene spacer in **1** by a *m*-pyridinediyl spacer.



Scheme 1

Results and discussion

Self-assembly of {2}-metalla-cryptates

Reaction of the *m*-pyridinediyl spacered ligands **3**[13,14] with iron(III) chloride and the corresponding guest cations M^{n+} afforded the {2}-metalla-cryptates $\{M\subset[Fe_2(\mathbf{3})_3]\}^{n+}$ M-**4** (Scheme 2).[12,15,16]

Structural investigations revealed that the pyridine groups of the *m*-pyridinediyl spacers strongly favour coordination of the M^{n+} cations in the macrobicyclic cavities. The FAB (fast atom bombardment)-MS spectra of the solid materials showed peaks at *m*/*z* 1294, 1559, 1237, and 1238, corresponding to the monocations $\{K\subset[Fe_2(\mathbf{3c})_3]\}^+$ K-**4c**, $\{K\subset[Fe_2(\mathbf{3d})_3]\}^+$ K-**4d**, the dication $\{Ba\subset[Fe_2(\mathbf{3a})_3]\}^{2+}$ Ba-**4a**, and the trication $\{La\subset[Fe_2(\mathbf{3a})_3]\}^{3+}$ La-**4a**. This indicated the formation of potassium-,

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† Chelate complexes. Part 16.[1] Dedicated to Ron Snaith. Electronic supplementary information (ESI) available: crystal structures of compounds K-**4d**, Ba-**4a** and La-**4a**. See http://www.rsc.org/suppdata/dt/b0/b008998m/

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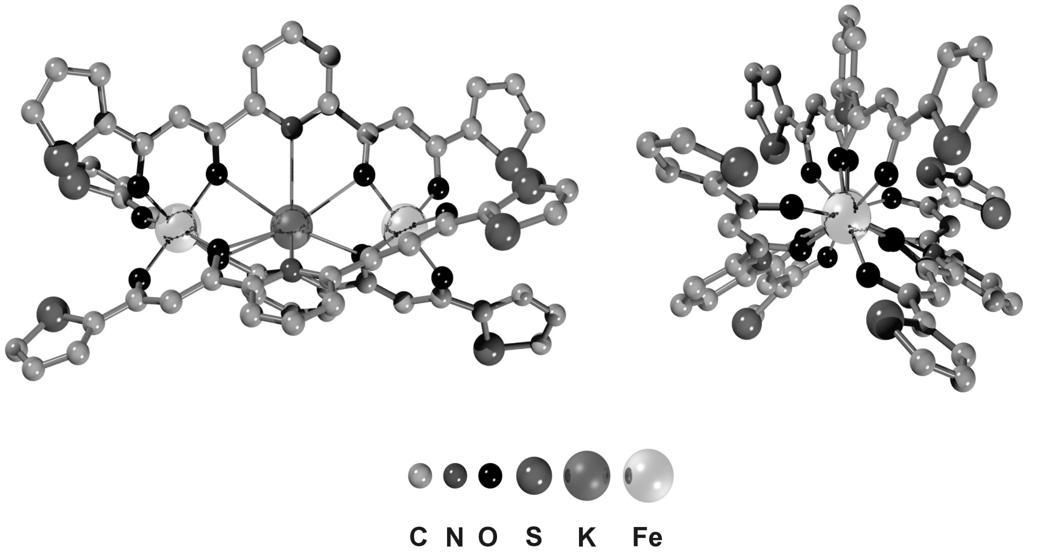
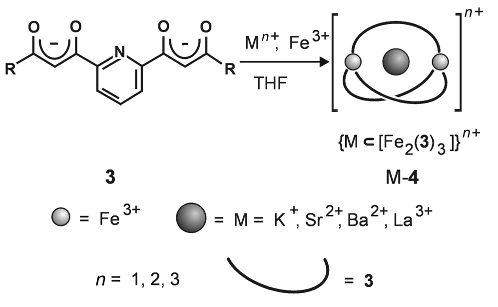


Fig. 1 Molecular structure of the cation $\{K\subset[Fe_2(\mathbf{3c})_3]\}^+$ of {2}-iron cryptate K-**4c**. Left: view perpendicular to the pseudo-C_3 axis. Right: view along the Fe–Fe axis. Hydrogen atoms, counter ions and solvent molecules omitted for clarity.



R / **3**, M-**4**	**a**	**b**	**c**	**d**
K-**4**	^{t}Bu^a	–	Thiophen	Naph
Sr-**4**	^{t}Bu^a	–	–	–
Ba-**4**	^{t}Bu	–	–	–
La-**4**	^{t}Bu	Me^a	–	–

^{a} Included for comparison: K-**4a**,[12] Sr-**4a** and La-**4b**.[15]

Scheme 2

barium- and lanthanum-containing {2}-metalla-cryptates. X-Ray crystallographic analyses were carried out for K-**4c**,**4d**, Ba-**4a** and La-**4a**. As an example, the molecular structure of K-**4c** is depicted in Fig. 1.[17]

Suitable crystals were obtained by diffusion of diethyl ether in a dichloromethane solution of compound K-**4c**. According to the structure determination, K-**4c** is present in the crystal as racemic (Δ,Δ)/(Λ,Λ)-$\{K\subset[Fe_2(\mathbf{3c})_3]\}^+$ {2}-iron cryptate. Additionally, one PF_6^- counter ion and three dichloromethane molecules are present in the unit cell. The potassium guest is nine-coordinated by six oxygen and three nitrogen atoms of the three ligands. The ligands are approximately octahedrally coordinated to the iron centers in a helical fashion. In the chiral complex of racemic K-**4c** both iron centers are identically coordinated. Therefore, K-**4c** is either a (Δ,Δ)-*fac* or (Λ,Λ)-*fac* {2}-iron cryptate. The iron–iron distance (7.01 Å) is slightly shorter than the corresponding distance observed in the potassium-containing iron cryptate K-**4a** (7.15 Å).[12]

Single crystals suitable for a structure determination were obtained by diffusion of diethyl ether into an acetone solution of compound K-**4d**. According to this analysis, K-**4d** is a racemic mixture of the helical (Δ,Δ)-*fac* and (Λ,Λ)-*fac* {2}-iron cryptates. The positive charge of the cluster is compensated by a $FeCl_4^-$ counter ion. Three acetone molecules are additionally present in the unit cell.

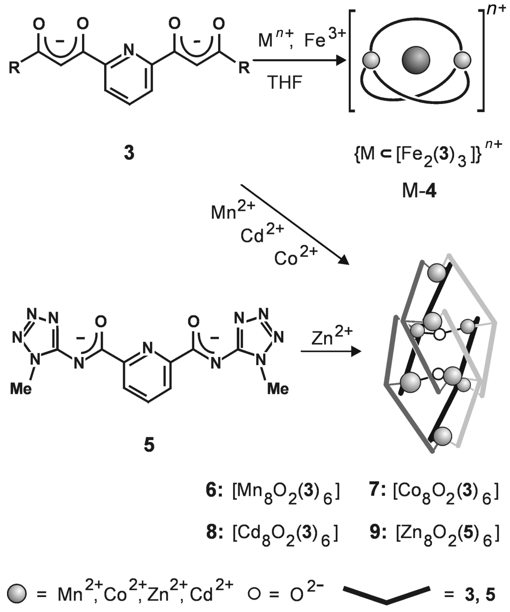
Dark red crystals of compound Ba-**4a** were obtained by diffusion of a mixture of hexanes and diethyl ether (1 : 1) in a THF solution of the complex. In this case barium is eleven-coordinated by six oxygen and three nitrogen atoms of the three ligands and two additional THF molecules, situated between each of the two ligand strands. The solvent molecules coordinate to the guest ion and are located in an almost perfect plane equatorially to the trigonal prism, formed by the oxygen atoms of the ligands. The metalla-cryptate Ba-**4a** is helical with either (Δ,Δ)-*fac* or (Λ,Λ)-*fac* coordinated iron centers, comparable to La-**4a**.

Octanuclear bis(triple-helical) metal(II) complexes

Reaction of the doubly negatively charged bis-bidentate ligands **3** with iron(III) chloride in the presence of alkaline, alkaline earth, and rare earth metal cations yielded the {2}-iron cryptates M-**4** with endohedral encapsulation of the mono-, di-, and tri-valent guest cations. In contrast, their reaction with transition metal cations Mn^{2+}, Co^{2+}, and Cd^{2+} revealed their pentadentate tritopic chelating nature to give the octanuclear complexes $[Mn_8O_2(\mathbf{3})_6]$ **6**,[16] $[Co_8O_2(\mathbf{3})_6]$ **7**, and $[Cd_8O_2(\mathbf{3})_6]$ **8**.[16] Similarly, the pentadentate tritopic ligand **5**, a topological equivalent of **3**, together with Zn^{2+} cations afforded the octanuclear cluster $[Zn_8O_2(\mathbf{5})_6]$ **9** (Scheme 3).[16] However, reaction of **5** with iron(III) chloride and alkaline, alkaline earth, and rare earth metal cations did not lead to the formation of type M-**4** products. With iron(III), ligand **5** reacted in its rotameric form, thus coordinating through five nitrogen donors to give the triple-helical, trinuclear, μ_3-oxo-centered mixed-valence iron complex $[Fe_3O(\mathbf{5}^{rot})_3]$.[18]

Upon reaction of ligand **3a** in THF with potassium carbonate, followed by cobalt(II) chloride, and subsequent work-up with dichloromethane, olive solid **7** was isolated. The FAB-MS spectrum displayed a peak at *m*/*z* 2479, corresponding to the composition $[Co_8O_2(\mathbf{3a})_6]$. Dark green needles of **7**, suitable for crystal structure analysis, were accessible from a methanolic solution of **7**. According to this analysis **7** is present in the crystal together with an undefined number of water molecules as the neutral, octanuclear bis(triple-helical) chelate complex $[Co_8O_2(\mathbf{3a})_6]$ (Fig. 2).

The core of complex **7** consists of eight cobalt(II) ions, forming a twofold capped, twisted trigonal prism with a μ_3-O^{2-} ion centered in each of the two inner faces. All the six doubly negatively charged pentadentate ligands **3a** link to three cobalt atoms. The two antipodal cobalt(II) ions are coordinated by three terminal and three μ_2-oxygen chelate atoms of three



R	3	4	6	7	8
a	^{t}Bu	^{t}Bu^a	^{t}Bu^a	^{t}Bu	^{t}Bu^a
b	Me	Me^a	Me^a	–	Me^a

^{a}Included for comparison: **4a**,[12] **4b**,[19] **6**, **8**.[16]

Scheme 3

ligands. However, the six metal centers, constituting the trigonal prism, are coordinated by one pyridinediyl nitrogen and two μ-chelate oxygen atoms. Distorted octahedral coordination of these six cobalt(II) ions is achieved by two extra μ_3-O^{2-} ions. Consequently, in the neutral, octanuclear, bis(triple-helical) complex **7** all the cobalt(II) ions are octahedrally coordinated. The core **7** is isostructural with those of **6**, **8** and **9**, but with greater distortion.

Conclusion

From the results of the structure determinations of the bicyclic metalla-cryptates M-**4** it is evident that their molecular structures are controlled by the nature of the endohedrally encapsulated cations and the specific ligands. It has been shown that {2}-metalla-cryptand **2** is a helicate, whereas {2}-metalla-cryptate K-**4a** is a mesocate.[12] However, helicity is not a characteristic feature of {2}-metalla-cryptands, since the {2}-metalla-cryptates K-**4c**,**4d** turned out to be helicates as well. Subtle peripheral changes of the ligands cause considerable torsional alterations. Currently, there is no general way rationally to design helicates or mesocates.

The corresponding europium cryptates {M⊂[Eu$_2$(**3**)$_3$]}$^{n+}$ display the typical luminescence of the europium cations after absorption of UV light by the ligand and energy transfer. The luminescence properties of these compounds are currently under investigation.

Experimental

Syntheses and characterization

The compounds **3** were prepared according to a literature procedure.[13,14] IR spectral data were recorded on a Bruker IFS 25, FAB mass spectra on a Micromass ZabSpec instrument using a 3-nitrobenzyl alcohol matrix. Microanalyses were performed on a Heraus CHN- and EA 1110 CHNS-Microautomat. THF was dried over sodium and distilled under a nitrogen atmosphere. The metal salts were used as purchased from Aldrich.

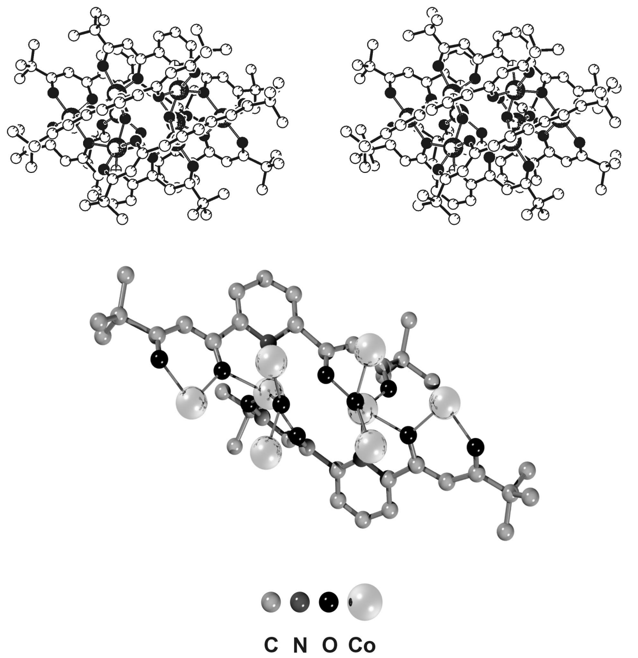


Fig. 2 Top: stereo view of the molecular structure of the octanuclear complex **7** in the crystal. Bottom: octanuclear core of **7** showing two ligands and the μ_3-O^{2-} ions. Hydrogen atoms and solvent molecules omitted for clarity.

General procedure for dinuclear iron(III) complexes M-4. To a solution of ligand **3** (1 mmol) in 75 ml of dry THF, 2 mmol of the metal carbonate was added. The mixture was stirred for 15 min at 20 °C. Iron(III) chloride (107 mg, 0.66 mmol) was then added, and the dark red solution stirred for 16 h at 20 °C. The solvent was removed *in vacuo* and the residue suspended in 50 ml of dichloromethane. After standing for 16 h at 20 °C, the red solution was filtered, the solvent removed, and the remaining crude product dried *in vacuo* (oil pump).

*{K⊂[Fe$_2$(**3c**)$_3$]}PF$_6$ K-**4c**.* Ruby-red needles were obtained by diffusion of diethyl ether into a dichloromethane solution of compound K-**4c**. Yield 411 mg (87%), mp >250 °C (decomp.) (Found: C, 47.56; H, 2.86; N, 2.89; S, 13.14%. $C_{57}H_{33}F_6Fe_2KN_3O_{12}PS_6$ requires C, 47.54; H, 2.31; N, 2.29; S, 13.36%). $\tilde{\nu}_{max}$/cm^{-1} (CHBr$_3$) 1529.9, 1504.9 (C=C) and 1307.6 (C–O). *m/z* 1294 ({K⊂[Fe$_2$L$_3$]}, 100) and 913 ({K⊂[Fe$_2$L$_2$]}, 98%).

*{K⊂[Fe$_2$(**3d**)$_3$]}FeCl$_4$·2C$_3$H$_6$O K-**4d**.* Ruby-coloured crystals were obtained by diffusion of diethyl ether into an acetone solution of compound K-**4d**. Yield 238 mg (42%), mp >250 °C (Found: C, 64.36; H, 4.08; N, 2.01%. $C_{102}H_{75}Cl_4Fe_3KN_3O_{15}$ requires C, 63.44; H, 3.91; N, 2.18%). $\tilde{\nu}$/cm^{-1} (CHBr$_3$) 1596.8, 1521.7, 1505.5 (C=C) and 1295.6 (C–O). *m/z* 1559 ({K⊂[Fe$_2$L$_3$]}, 98) and 1089 ({K⊂[Fe$_2$L$_2$]}, 100%).

*{Ba⊂[Fe$_2$(**3a**)$_3$]}[FeCl$_4$]$_2$ Ba-**4a**.* Ruby-coloured crystals were obtained by diffusion of a mixture of diethyl ether and hexanes (1 : 1) into a THF solution of compound Ba-**4a**. Yield 268 mg (99%), mp >250 °C (decomp.) (Found: C, 40.38; H, 4.27; N, 2.58%. $C_{57}H_{69}BaCl_8Fe_4N_3O_{12}$ requires C, 41.94; H, 4.26; N, 2.57%).[20] $\tilde{\nu}$/cm^{-1} (CHBr$_3$) 2964.9 (CH$_3$), 1553.7, 1513.8 (C=C), 1386.9 (CH$_3$) and 1315.2 (C–O). *m/z* 1435 ({Ba⊂[Fe$_2$L$_3$]} + FeCl$_4$, 53), 1237 ({Ba⊂[Fe$_2$L$_3$]}, 100), 1180 ({Ba⊂[Fe$_2$L$_3$]} − ^{t}Bu, 18) and 978 ({Ba⊂[Fe$_2$L$_2$]} + 2Cl, 44%).

*{La⊂[Fe$_2$(**3a**)$_3$]}[FeCl$_4$]$_3$ La-**4a**.* Ruby-coloured crystals were obtained by diffusion of diethyl ether into a dichloromethane solution of compound La-**4a** Yield 223 mg (92%), mp >250 °C (decomp.) (Found: C, 33.42; H, 4.24; N, 1.41%. $C_{57}H_{69}Cl_{12}Fe_5LaN_3O_{12}$ requires C, 37.38; H, 3.80; N, 2.29%).[20] $\tilde{\nu}$/cm^{-1} (CHBr$_3$) 2973.2 (CH$_3$), 1593.1, 1510.8 (C=C) and 1296.9 (C–O). *m/z* 1471 ({La⊂[Fe$_2$L$_3$]} + FeCl$_4$ + Cl, 18), 1273 ({La⊂[Fe$_2$L$_3$]} + Cl, 100), 1238 ({La⊂[Fe$_2$L$_3$]}, 49) and 979 ({La⊂[Fe$_2$L$_2$}] + THF, 77%).

Table 1 Crystallographic data for compounds K-**4c**, Ba-**4a** and La-**4a**

	K-**4c**	Ba-**4a**	La-**4a**
Formula[a]	$C_{60}H_{39}Cl_6F_6Fe_2KN_3O_{12}PS_6$	$C_{65.25}H_{85.5}BaCl_{8.5}Fe_4N_3O_{14}$	$C_{69.5}H_{104}Cl_{13}Fe_5LaN_3O_{17}$
M	1694.77	1797.93	2132.57
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	12.114(3)	17.835(4)	14.792(2)
b/Å	17.853(3)	22.145(3)	16.969(3)
c/Å	31.886(4)	22.985(4)	20.647(3)
α/°		112.21(2)	68.83(2)
β/°	100.55(1)	94.67(2)	84.05(2)
γ/°		94.07(2)	75.21(2)
V/Å^3	6779(2)	8330(10)	4672(1)
Z	4	4	2
μ/mm^{-1}	1.013	1.475	1.633
Reflections measured	16301	30685	78110
Unique reflections	13310	25032	19088
R_{int}	0.0441	0.0729	0.0706
R	0.069	0.082	0.045
$wR(F^2$, all data)	0.189	0.246	0.097

[a] Crystal solvent included.

[Co$_8$O$_2$(3a)$_6$] 7. Compound **7** was obtained according to the general procedure, but by heating the THF solution of ligand **3a**, potassium hydride and cobalt(II) chloride for 18 h under reflux instead of stirring the THF solution for 16 h at 20 °C. Dark green needles were obtained by crystallization from methanol. Yield 657 mg (79%), mp >250 °C (decomp.) (Found: C, 55.61; H, 5.89; N, 3.71%. $C_{114}H_{138}Co_8N_6O_{26}$ requires C, 55.22; H, 5.61; N, 3.39%). $\tilde{\nu}_{max}$/cm^{-1} (CHBr$_3$) 2963.1, 2902.9, 2868.2 (CH$_3$), 1615.2, 1590.9, 1510.8 (C=C), 1389.7 (CH$_3$) and 1293.2 (C–O). *m*/*z* 2479 ([Co$_8$O$_2$L$_6$], 100%).

Crystal structure determination

Details of the structure determinations are given in Table 1. Crystals of the compounds were examined at 200 K on a Siemens P4 diffractometer and for La-**4a** at 130 K on a Stoe-Siemens-Huber four-circle diffractometer with a Siemens SMART CCD detector using Mo-Kα radiation (λ = 0.71073 Å, graphite monochromator). Data were corrected for Lorentz and polarization effects. Absorption effects have been accounted for using ψ scans (K-**4c**, Ba-**4a**) or equivalents (La-**4a**). All structures were solved by direct methods (La-**4a**: SHELXS 97[21]) and refined either by full-matrix least squares procedures (K-**4c**) or using a blocked-matrix refinement (Ba-**4a**) against F^2 (SHELXTL NT 5.1[22] for K-**4c** and Ba-**4a**, SHELXL 97[23] for La-**4a**). The hydrogen atoms of K-**4c** and Ba-**4a** were calculated in idealized positions and allowed to ride on their corresponding carbon atoms, their isotropic thermal parameters being tied to those of the adjacent carbon atoms by a factor of 1.2 or 1.5. In La-**4a** the hydrogen atoms bound to oxygen atoms were refined freely with distance restraints. Some of the *t*-butyl groups in La-**4a**, the $FeCl_4^-$ anions and part of the solvent (three diethyl ether and one methylene chloride) are disordered. These groups were refined with distance restraints and restraints for the anisotropic displacement parameters. Selected bond distances and angles are summarized in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) of compounds K-**4c**, Ba-**4a** and La-**4a**

	K-**4c**	Ba-**4a**	La-**4a**
M(1)–O(1)	2.850(4)	2.749(6)	
M(1)–O(12)			2.616(3)
M(1)–O(3)	2.724(5)	2.751(6)	
M(1)–O(13)			2.824(3)
M(1)–N(1)	2.958(5)	2.877(8)	2.865(3)
M(1)···Fe(1)	3.513(2)	3.577(2)	3.556(9)
M(1)···Fe(2)	3.500(2)	3.600(2)	3.586(2)
Fe(1)–O(1)	2.015(4)	2.009(7)	
Fe(1)–O(12)			1.990(3)
Fe(1)–O(2)	1.989(4)	1.969(8)	
Fe(1)–O(11)			1.964(3)
Fe(2)–O(3)	1.999(4)	2.039(6)	
Fe(2)–O(13)			1.990(3)
Fe(2)–O(4)	1.983(4)	1.948(7)	
Fe(2)–O(14)			1.948(3)
M(1)–O(120)		3.001(8)	
M(1)–O(2)			2.528(3)
Fe(1)···Fe(2)	7.013(1)	7.176(5)	7.140
Fe(2)–M(1)–Fe(1)	178.4(5)	178.5(3)	176.5(8)
N(2)–M(1)–N(1)	128.8(2)	122.4(2)	130.0(9)
N(3)–M(1)–N(1)	115.6(2)	127.2(2)	130.4(1)
O(2)–Fe(1)–O(1)	85.6(2)	83.8(3)	84.6(1)
O(4)–Fe(2)–O(3)	83.9(2)	84.6(3)	86.9(1)
O(1)–M(1)–N(1)	55.3(2)	57.1(2)	55.8(9)
O(3)–M(1)–N(1)	54.0(2)	56.1(2)	54.7(9)
O(3)–M(1)–O(1)	108.7(2)	113.2(2)	110.0(8)

The poor crystal quality and the weak diffracting power of crystalline compounds K-**4d** and **7** allowed only partial structure determination in these cases. In particular, there are voids in the crystal structures that are most likely occupied by highly disordered solvent. Attempts to locate well resolved solvent molecules met with partial success in the case of K-**4d**, where 3 molecules of acetone were identified. 14 electron density maxima were tentatively assigned to oxygen atoms of water molecules in the case of **7**. All further attempts to locate solvent molecules in either K-**4d** or **7** were unsuccessful. Therefore, the refinements of K-**4d** and **7** do not allow detailed discussion. However, the connectivity and other broad structural features of the main complex are well refined and undoubtedly correct. The crystal data determined so far are: K-**4d**, $C_{83}H_{57}Cl_4Fe_3KN_3O_{12}\cdot 3C_3H_6O$, trigonal, space group $P\bar{3}$, $a = b = 16.179(3)$, $c = 20.981(4)$ Å, $V = 4756(2)$ Å^3, $Z = 2$, $R1$ ($I > 2\sigma(I)) = 0.129$, $wR2$ (all data) = 0.349; **7**, $C_{114}H_{138}Co_8N_6O_{26}\cdot 27H_2O$, monoclinic, space group $C2/c$, $a = 26.001(6)$, $b = 31.448(7)$, $c = 20.135(7)$ Å, $\beta = 103.78(2)°$, $V = 15990(8)$ Å^3, $Z = 4$, $R1$ ($I > 2\sigma(I)) = 0.149$, $wR2$ (all data) = 0.379.

CCDC reference numbers 152453–152457.

See http://www.rsc.org/suppdata/dt/b0/b008998m/ for crystallographic data in CIF or other electronic format.

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